

## [Bis(3,5-dimethylpyrazol-1-yl- $\kappa N^2$ )-hydro(pyrazol-1-yl- $\kappa N^2$ )borato][(3,5-dimethylpyrazol-1-yl- $\kappa N^2$ )dihydro(pyrazol-1-yl- $\kappa N^2$ )borato]nickel(II)

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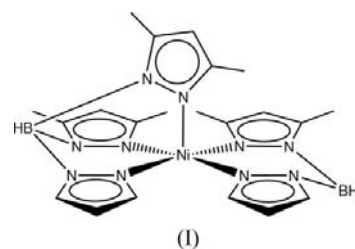
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The title compound,  $[\text{Ni}(\text{C}_8\text{H}_{12}\text{BN}_4)(\text{C}_{13}\text{H}_{18}\text{BN}_6)]$  or  $\text{Bp}'\text{Tp}'\text{-Ni}^{\text{II}}$ , where  $\text{Bp}'$  is (3,5-dimethylpyrazol-1-yl)dihydro(pyrazol-1-yl)borate and  $\text{Tp}'$  is bis(3,5-dimethylpyrazol-1-yl)hydro(pyrazol-1-yl)borate, contains a divalent  $\text{Ni}^{\text{II}}$  centre bound by the chelating N atoms of the polysubstituted pyrazolylborate ligands. It is shown to lack a strong agostic  $\text{B}-\text{H}\cdots\text{Ni}$  interaction, implying that the sixth coordination site is unoccupied in the solid state. This square-pyramidal complex is the only known crystal structure where the  $\text{Ni}^{\text{II}}$  centre is pentacoordinated while bonded exclusively to pyrazolyl units. This is of interest with respect to electrochemical and catalytic properties.

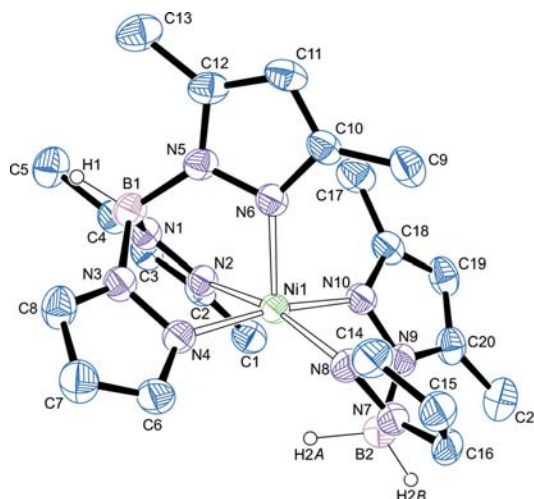
### Comment

Polypyrazolylborate ligands, also known as scorpionate ligands, are a unique class of ligands that have been extensively studied, in part because they are known to adopt multiple bonding configurations. The most common ones are the bidentate  $\kappa^2\text{N},\text{N}'$  and tridentate  $\kappa^3\text{N},\text{N}',\text{N}''$  types, while  $\kappa^1\text{N}$ ,  $\kappa^2\text{H},\text{N}$  and  $\kappa^3\text{H},\text{N},\text{N}'$  types are also known (Belderrain *et al.*, 2002). Our interest in this class of compounds lies in the change in coordination geometry that can be induced through oxidation of the central ion (Connelly *et al.*, 2001; Geiger *et al.*, 2003). Specifically, this structural change may be exploited to modify the potential difference between subsequent oxidation states, thereby in theory yielding access to the coveted two-electron transfer. The nomenclature adopted here is as recommended by Trofimenko (1999). Thus, bis- and tris-(homopyrazolyl)borate ligands are represented by the abbreviations Bp and Tp, respectively. The 3- and 5-alkyl substituents located on the pyrazolyl rings are listed in this order as superscripts, unless otherwise specified [*e.g.*  $\text{Bp}^{4\text{CN}} = [\text{H}_2\text{B}(4\text{-cyanopyrazolyl})_2]^-$ ]. In addition, the abbreviations  $\text{py} = \text{pyrazolyl}$ ,  $\text{dmpz} = 3,5\text{-dimethylpyrazolyl}$  and  $\text{dppz} = 3,5\text{-diphenylpyrazolyl}$  are used.

The title compound, (I) (Fig. 1), was isolated while attempting to prepare the  $\text{Tp}'_2\text{Ni}$  scorpionate complex, where  $\text{Tp}''$  is  $[(3,5\text{-dimethylpyrazolyl})(\text{pyrazolyl})_2\text{BH}]^-$ . Compound (I), generated *in situ* alongside the known orange-coloured  $\text{Bp}'_2\text{Ni}^{\text{II}}$  complex (Frauendorfer & Agrifoglio, 1982), consists of a pentahedral  $\text{Ni}^{\text{II}}$  centre bound by the five pyrazolyl groups of the combined  $\text{Bp}'$  and  $\text{Tp}'$  ligands. The mechanism driving the *in situ* rearrangement of  $\text{Tp}''$  to form the  $\text{Bp}'$  and  $\text{Tp}'$  ligands in the presence of nickel is still under investigation. Hence, it will not be considered here.



A survey of the literature revealed (I) to be the only structurally characterized example of a mixed  $\text{Bp}-\text{Tp}$ -type nickel complex. However, analogous cobalt(II) complexes have been shown to adopt either a pentahedral [*e.g.*  $[\text{Tp}^{\text{CHPh}_2}][\text{Ph}_2\text{Bp}]\text{Co}$  (Rheingold *et al.*, 2004),  $[\text{Tp}^{i\text{-Pr},4\text{Br}}][\text{Ph}_2\text{Bp}]\text{Co}$  (Calabrese *et al.*, 1990) and  $[\text{Bp}^{4\text{CN}}][\text{Tp}^{\text{Np}}]\text{Co}$  (Rheingold *et al.*, 2000)] or an octahedral [*e.g.*  $[\text{Tp}^{\text{CHPh}_2}][\text{Bp}^{\text{Ph}}]\text{Co}$  (Rheingold *et al.*, 2004),  $[\text{Tp}^{i\text{-Pr},4\text{Br}}][\text{Bp}^{\text{Ph}}]\text{Co}$  (Calabrese *et al.*, 1990),  $[\text{Bp}^{\text{Ph},\text{Ph}}][\text{HB}(3,5\text{-dmpz})_2(3,5\text{-dppz})]\text{Co}$  (Ruman *et al.*, 2001) and  $[\text{Bp}^{\text{Ph},\text{Ph}}][\text{HB}(3,5\text{-dppz})_2(3,5\text{-dmpz})]\text{Co}$  (Ruman *et al.*, 2002)] geometry, depending on their ability to form a  $\kappa^3\text{N},\text{N},\text{H}$  agostic interaction. Exceptionally,  $[\text{Bp}^{4\text{CN}}][\text{Tp}^{\text{Cy}}]\text{Co}$  (Cy is cyclohexyl) is square pyramidal in solution, but octahedral when crystallized from a dimethylformamide solution (Rheingold *et al.*, 2000). Moreover, Jezorek & McCurdy (1975) found that octahedral  $[\text{Bp}_3\text{Ni}]^-$  could be isolated from solutions kept meticulously anhydrous, whereas any exposure to moisture reverts the complex to the common



**Figure 1**  
The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Carbon-bound H atoms have been omitted for clarity.

Bp<sub>2</sub>Ni form that contains no metal-coordinated water. Combined, these results illustrate the delicate energy differences that exist between the different coordination modes of Bp- and Tp-type ligands. In turn, it is the possibility of controlling this energy by judicious choice of ligand geometry that makes this class of compounds ideal for the design of redox-dependent coordination geometries. To this end, the detailed geometry of (I) is crucial.

The shortest Ni–N bond length (Table 1) of (I) was found to be the apical dmpz moiety of the Tp' ligand (*i.e.* Ni1–N6), whereas the other Ni–N bonds, which define the square plane, are of similar length ( $\sim 2.06$  Å) within the range of experimental error ( $3\sigma$ ). These values are slightly shorter than the Ni–N bonds found in the octahedral Tp<sub>2</sub>Ni<sup>II</sup> complex [2.087 (2)–2.104 (3) Å; Bandoli *et al.*, 1979], but considerably longer than the Ni–N bonds of the square-planar *trans*-Bp'<sub>2</sub>Ni<sup>II</sup> complex [1.894 (2) and 1.883 (3) Å; Kokusen *et al.*, 1996]. This suggests an important steric/electronic effect by the apical dmpz unit in (I). In addition, the Ni<sup>II</sup> ion is found to be 0.2009 (4) Å above the square plane defined by atoms N2, N4, N8 and N10, indicating an attraction to the apical dmpz moiety.

Determining whether or not an agostic B–H...Ni bond is present in (I) is important, since the absence of such a bond implies that one coordination site remains open for reaction. Belderrain *et al.* (2002) found that the length of the B–H bond of Ni[Bp'<sup>t-Bu</sup>]<sub>2</sub> implicated in the agostic interaction is 1.26 (5) Å, whereas the uncoordinated B–H bond is 1.15 (5) Å. This is similar to the bond lengths of B2–H2A and B2–H2B (Table 1). In addition, these bonds are unequal in length in (I), as would be expected if an agostic interaction is present. However, the (B)H...Ni distance in (I) is 2.59 Å, considerably longer than those found in complexes with confirmed agostic-type interactions, *e.g.* [Ni(NCBH<sub>3</sub>)<sub>2</sub>(2,2',2''-triaminotriethylamine)]<sub>2</sub><sup>+</sup> [2.15 (3) Å; Segal & Lippard, 2002] and Ni[Bp'<sup>t-Bu</sup>]<sub>2</sub> [1.86 (5) Å; Belderrain *et al.*, 2002]. To examine this effect further, the B...Ni distance is analysed. This distance is an indirect measure of the agostic interaction, since H...Ni bonding requires the approach of the BH unit to the central Ni atom, thereby inducing strain in the N–Ni bond due to the rigid nature of the pyrazolyl unit. Comparison of the B...Ni distance in (I) (3.00 Å) with that observed in compounds exhibiting and devoid of agostic interactions, *e.g.* Ni[Bp'<sup>t-Bu</sup>]<sub>2</sub> (2.54 Å; Belderrain *et al.*, 2002) and Bp'<sub>2</sub>Ni (3.05 Å; Kokusen *et al.*, 1996), respectively, suggests that the (B)H...Ni bond is very weak or possibly absent in (I).

The encapsulation of the metal ion by ligands provides it with the steric restraint necessary to avoid unwanted dissociation, substitution and dimerization reactions often seen during redox and/or catalytic cycling. Conversely, a totally impenetrable capsule renders the central ion chemically inert. A quantitative measure by which to compare the degree of enclosure of different coordination and organotransition metal complexes is the wedge angle (Bondi, 1964). This defines the unoccupied space around the metal core accessible to an approaching solvent or substrate molecule and takes into account the van der Waals radii of the selected atoms. An

appropriate measure is to determine both the widest and the narrowest wedge angles. The former, the wedge angle between the Tp'-bound B atom, the Ni core and the closest Bp'-bound H atom (*i.e.* B1–Ni1–H2B), is 87°. The latter, the wedge angle between the 3'-Me group of the Tp'-bound pyrazolyl ligand, the Ni core and the 3'-H atom of the adjacent unsubstituted Tp'-bound pyrazolyl ligand (*i.e.* H1C–Ni1–H6), is 68°. By comparison, the related wedge angles of the *trans*-Bp'<sub>2</sub>Ni<sup>II</sup> complex (Kokusen *et al.*, 1996) were calculated as 112 and 59°, respectively. Note that in the latter case these wedge angles can be measured from both top and bottom hemispheres.

The wedge angle is of further importance here as the introduction of a highly nucleophilic ligand opposite the apical dmpz unit should weaken the Ni1–N6 bond, as is the case in the classical Tp<sub>2</sub>Ni complex. In the extreme case, where this ligand addition leads to cleavage of the Ni1–N6 bond, a pendent pyrazolyl unit is formed. Upon oxidation, this unit will be prone to (re)coordination with the central Ni<sup>II</sup> ion. The addition of a ligand in the vacant sixth coordination site would therefore be a route towards complexes that exhibit redox-dependent coordination geometry. This approach is currently under study in our laboratory.

In summary, our study reports the geometric parameters of the first pentahedral mixed Bp'–Tp' nickel coordination complex. We find no evidence for a strong agostic B–H...Ni interaction, hence conserving a free coordination site in the solid state despite the absence of large substituents on the pyrazolyl units. A measure of the wedge angles indicates that, similar to Bp<sub>2</sub>Ni-type complexes but to a lesser degree, the Ni core is exposed. This offers a lead for further modification of this class of complexes.

## Experimental

The NaTp'' complex was synthesized in a stepwise fashion by the condensation of an equimolar amount of 3,5-dimethylpyrazole with pure NaBp in refluxing anisole. The progress of the reaction was monitored by measuring the volume of H<sub>2</sub> gas that evolved. Once completed, the product was used for complexation without further purification.

The dropwise addition of a lime-green aqueous solution (10 ml) of NiCl<sub>2</sub>(H<sub>2</sub>O)<sub>6</sub> (0.357 g, 1.50 mmol) to a stirred colourless heterogeneous solution composed of H<sub>2</sub>O (10 ml), dichloromethane (20 ml) and the NaTp'' complex (0.792 g, 3.00 mmol) resulted in the formation of a red mixture. Following 10 min of further stirring, the organic phase was isolated and the aqueous phase was washed with three portions of dichloromethane (10 ml). The combined organic extracts were dried over MgSO<sub>4</sub>, filtered and concentrated slowly under reduced pressure. During this time, an orange precipitate gradually appeared and the resulting mother liquor progressively turned a pale-violet colour. Filtration and complete evaporation of the solvent produced a violet crystalline solid. This crude material was further purified from the orange Bp'<sub>2</sub>Ni<sup>II</sup> by-product by flash chromatography using silica gel and an eluent mixture of 10% ethyl acetate in hexanes. Nevertheless, <sup>1</sup>H NMR and liquid chromatography–high-resolution mass spectroscopy suggested that more than one species was present in the isolated band. Pale-pink (almost colourless) crystals of (I) were

obtained by slow evaporation from a dichloromethane solution of the violet product (over a period of *ca* 3 d) at ambient temperature.

## Crystal data

[Ni(C <sub>8</sub> H <sub>12</sub> BN <sub>4</sub> )(C <sub>13</sub> H <sub>18</sub> BN <sub>6</sub> )]	$V = 2510.87 (9) \text{ \AA}^3$
$M_r = 502.86$	$Z = 4$
Monoclinic, $P2_1/c$	Cu $K\alpha$ radiation
$a = 15.1899 (3) \text{ \AA}$	$\mu = 1.35 \text{ mm}^{-1}$
$b = 9.8327 (2) \text{ \AA}$	$T = 298 \text{ K}$
$c = 17.1131 (4) \text{ \AA}$	$0.30 \times 0.10 \times 0.05 \text{ mm}$
$\beta = 100.780 (1)^\circ$	

## Data collection

Bruker Microstar diffractometer	41333 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4574 independent reflections
$T_{\min} = 0.758, T_{\max} = 0.935$	3344 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.063$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.142$	$\Delta\rho_{\max} = 0.53 \text{ e \AA}^{-3}$
$S = 1.03$	$\Delta\rho_{\min} = -0.23 \text{ e \AA}^{-3}$
4574 reflections	
322 parameters	

**Table 1**

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Ni1—N2	2.055 (2)	Ni1—N10	2.058 (2)
Ni1—N4	2.063 (2)	B1—H1	1.10 (3)
Ni1—N6	2.038 (2)	B2—H2A	1.26 (3)
Ni1—N8	2.068 (2)	B2—H2B	1.13 (3)
N2—Ni1—N4	87.58 (8)	N4—Ni1—N6	88.31 (9)
N2—Ni1—N6	92.39 (8)	N4—Ni1—N10	170.87 (9)
N2—Ni1—N8	166.66 (9)	N6—Ni1—N8	100.62 (9)
N2—Ni1—N10	91.53 (9)	N6—Ni1—N10	100.80 (9)
N4—Ni1—N8	89.83 (8)	N8—Ni1—N10	88.97 (9)

H atoms bonded to C atoms were treated as riding, with C—H = 0.93–0.97  $\text{\AA}$ , and with  $U_{\text{iso}}(\text{H}) = kU_{\text{eq}}(\text{C})$ , where  $k = 1.5$  for the methyl groups, which were permitted to rotate but not to tilt, and 1.2 otherwise. The coordinates of the H atoms bonded to B atoms were refined freely, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{B})$ , giving B—H distances in the range 1.10 (3)–1.26 (3)  $\text{\AA}$ . A slightly unusual orientation was observed for the displacement ellipsoids along the C15—C16 bond. This effect diminishes at lower temperature. The displacement parameter  $U_{\text{eq}}$  takes the values 0.069, 0.070 and 0.068  $\text{\AA}^2$  for atoms C14, C15 and C16, respectively. Since all of these atoms are part of a preformed pyrazolyl unit, incorrect atom assignment seems improbable.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *UdMX* (Maris, 2004).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3299). Services for accessing these data are described at the back of the journal.

## References

- Bandoli, G., Clemente, D. A., Paolucci, G. & Doretti, L. (1979). *Cryst. Struct. Commun.* **8**, 965–970.
- Belderráin, T. R., Paneque, M., Carmona, E., Gutiérrez-Puebla, E., Monge, A. & Ruiz-Valero, C. (2002). *Inorg. Chem.* **41**, 425–428.
- Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.
- Bruker (2007). *SAINT*. Version 7.34A. Bruker AXS Inc., Madison, Wisconsin, USA.
- Bruker (2008). *APEX2*. Version 2.1.0. Bruker AXS Inc., Madison, Wisconsin, USA.
- Calabrese, J. C., Domaille, P. J., Thompson, J. S. & Trofimenko, S. (1990). *Inorg. Chem.* **29**, 4429–4437.
- Connelly, N. G., Emslie, D. J. H., Geiger, W. E., Hayward, O. D., Linehan, E. B., Orpen, A. G., Quayle, M. J. & Rieger, P. H. (2001). *J. Chem. Soc. Dalton Trans.* pp. 670–683.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Frauentorfer, E. & Agrifoglio, G. (1982). *Inorg. Chem.* **21**, 4122–4125.
- Geiger, W. E., Ohrenberg, N. C., Yeomans, B., Connelly, N. G. & Emslie, D. J. H. (2003). *J. Am. Chem. Soc.* **125**, 8680–8688.
- Jezorek, J. R. & McCurdy, W. H. (1975). *Inorg. Chem.* **14**, 1939–1944.
- Kokusen, H., Sohrin, Y., Matsui, M., Hata, Y. & Hasegawa, H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 195–201.
- Maris, T. (2004). *UdMX*. Université de Montréal, Canada.
- Rheingold, A. L., Incarvito, C. D. & Trofimenko, S. (2000). *Inorg. Chem.* **39**, 5569–5571.
- Rheingold, A. L., Liable-Sands, L. M., Golen, J. A., Yap, G. P. A. & Trofimenko, S. (2004). *Dalton Trans.* pp. 598–604.
- Ruman, T., Ciunik, Z., Gočan, A., Łukasiewicz, M. & Wołowicz, S. (2001). *Polyhedron*, **20**, 2965–2970.
- Ruman, T., Ciunik, Z., Mazurek, J. & Wołowicz, S. (2002). *Eur. J. Inorg. Chem.* pp. 754–760.
- Segal, B. G. & Lippard, S. J. (2002). *Inorg. Chem.* **16**, 1623–1629.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Trofimenko, S. (1999). *Scorpionates: The Coordination Chemistry of Polypyrazolylborate Ligands*. London: Imperial College Press.